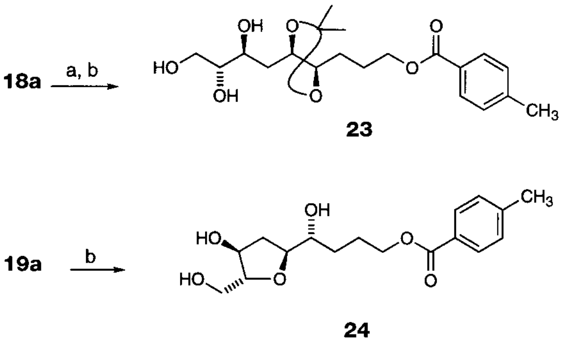
no selectivity clearly indicates that the stereogenic centers of the substrate are unsuitable for acyclic stereocontrol.

Can one dispose of the workbench after the job is done? As exemplified for the dihydroxylation product **18a,** the benzyl acetal can not be hydrolyzed under mild acid catalysis, but is easily cleaved hydrogenolytically (Scheme 3). Thus one obtains the partially protected hexol derivative **23**; the arene remains bonded to one of the primary hydroxy groups as the 4-methyl benzoate protecting group. Epoxides such as **19a** are transformed into tetrahydrofuran derivatives (e.g. **24**) by an S_N2 attack of the hydroxy group liberated after debenzylation. The arene **9** that is incorporated into the macrolide can therefore be understood as a polyfunctional protecting group that amplifies the influence of the substrate's stereogenic centers. As such it thus represents a new type of "stereoactive protective group".[7]



Scheme 3. Cleavage of the "workbench". a) 2,2-dimethoxypropane, PPTS, CH_2Cl_2, 94%; b) H_2/Pd/C, EtOAc; **23** 97%, **24** 97%. PPTS = pyridinium-*p*-toluene sulfonate.

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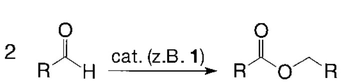
Homoleptic Lanthanide Amides as Homogeneous Catalysts for the Tishchenko Reaction[**]

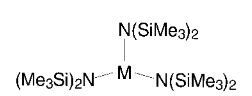
Helga Berberich and Peter W. Roesky[*]

The Tishchenko reaction (or Claisen–Tishchenko reaction), that is, the dimerization of aldehydes to form the corresponding carboxylic ester [Eq. (1)], has been known for about a century.[1] Its industrial importance is mirrored in the great number of patents. Thus the Tishchenko ester of 3-cyclohexenecarbaldehyde is the precursor for the formation of epoxy resin, which is durable against environmental influences.[2] Traditionally aluminum alkoxides[2a, 3] have been used as homogeneous catalysts for the catalytic variations of the Tishchenko reaction. More recently other catalysts such as boric acid[4] and a few transition metal complexes[5] are used. However, these alternative catalysts are either only reactive under extreme reaction conditions (e.g. boric acid), difficult to prepare (e.g. $[(C_5Me_5)_2LaCH(SiMe_3)_2]$),[5a] slow (e.g. $[(C_5H_5)_2ZrH_2]$),[5b] expensive (e.g. $[H_2Ru(PPh_3)_2]$),[5c] or give small yields (e.g. $K_2[Fe(CO)_4]$).[5d]



(1)

Herein we report that the homoleptic bis(trimethylsilyl) amides of Group 3 metals and lanthanides, $M[N(SiMe_3)_2]_3$[6] **1** (M = Sc, Y, Ln (lanthanide)), are highly active catalysts for the Tishchenko reaction. Compound **1** belongs to a class of materials that has been known for the last 25 years. Recently, in particular, it has proven to be a valuable starting material in lanthanide chemistry through the easy cleavage of the silylamide group.[7] Compound **1** can either be prepared from a simple one-step synthesis or it can be bought (M = Y). Therefore it is even more surprising to find that up till now there is no known use of **1** as a catalyst.



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To compare the reaction rates of **1** with other catalysts the standard reaction of benzaldehyde to benyzl benzoate was

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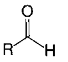
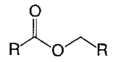
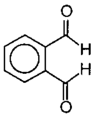
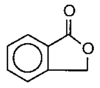
chosen, whereby the reaction rate and the yield were determined by NMR spectroscopy in C_6D_6 with approximately 1 mol% catalyst at 21 °C (Table 1). The turnover frequencies (TOFs) were determined from a turnover of 50% (see below). A comparison of $La[N(SiMe_3)_2]_3$ (**1a**), $Sm[N(SiMe_3)_2]_3$ (**1b**), and $Y[N(SiMe_3)_2]_3$ (**1c**) shows that by almost quantitative turnover **1a** has a higher activity than the corresponding Sm catalyst **1b**, whereas the Y catalyst **1c** produces smaller yields and is less active. The dependence of the TOF on the ionic radius of the central metal atom has already been observed.[5a] A comparison with other easily accessible lanthanide compounds such as SmI_2[8] or La(O*i*Pr)$_3$,[5a] which are used as Tishchenko catalysts, showed that these are inactive for the case of benzaldehyde. From the reaction with the standard aluminum catalyst (Al(O*i*Pr)$_3$),[3] under the reaction conditions described above, no quantitative yield was observed. The reaction rate observed with the use of Al(O*i*Pr)$_3$, which agrees with earlier measured values,[3a, 9] is roughly an order of magnitude smaller than that when **1a** is used. Although we do not know of a more active catalyst for the Tishchenko reaction, two compounds are described in the literature ($[(C_5Me_5)_2LaCH(SiMe_3)_2]$[5a] and $Al(OCH_2Ph)_3$[9]) that could compete with **1a**. $[(C_5Me_5)_2LaCH(SiMe_3)_2]$ probably would form the same catalytically active species as in **1a** (see below), but is, however, evidently more difficult to prepare. $Al(OCH_2Ph)_3$ reaches almost the same TOF as **1a**, but is exclusively optimized for the dimerization of benzaldehyde.[9, 10]

Table 1. Catalytic Tishchenko reaction of benzaldehyde to benzyl benzoate.

Catalyst	TOF	Yield [%]	*T* [°C]	Ref.
1a	87	98	21	–[a]
1b	80	98	21	–[a]
1c	63	70	21	–[a]
$[(C_5Me_5)_2LaCH(SiMe_3)_2]$		88	RT	[5a]
SmI_2	–	no reaction	21	–[a]
La(O*i*Pr)$_3$	–	no reaction	60	[5a]
Al(O*i*Pr)$_3$	8	51	21	–[a]
$[(C_5H_5)_2ZrH_2]$		7	17	[5b]
$[(C_5H_5)_2HfH_2]$		9	17	[5b]
$[H_2Ru(PPh_3)_2]$		23	20	[5c]
$K_2[Fe(CO)_4]$		71	60	[5d]
$B(OH)_3$		34	250	[4]

[a] Reaction conditions (this work): 1 mol% catalyst in C_6D_6.

Table 2. Catalytic Tishchenko reaction with **1a** as the catalyst.

Reactant	Product	TOF	Yield [%][a]	Yield [%][b]
				
R = phenyl		87	98	87
R = 3-cyclohexenyl		> 1500	quant.	75
R = cyclohexyl		> 1500	quant.	80
R = 2-furanyl		2	40	36
R = 1-propyl		–	quant.[c]	45[c,d]
		> 1500	90[e]	85[d]

[a] Analytical approach (NMR experiment): 21 °C, 1 mol% catalyst in C_6D_6. [b] Yield of isolated product for the preperative approach: 21 °C, 5 g of reactant, 1 mol% catalyst, no solvent. [c] Reaction from – 78 °C → RT; trimers were formed as by-products. [d] Solvent: 50 mL of pentane/hexane (1/1). [e] Unknown by-product.

The large range of applications of **1a** is given in Table 2. The reactions were carried out at 21 °C in C_6D_6 with approximately 1 mol% of catalyst in order to determine the TOF. Afterwards all the reactions were repeated on a preparative scale (5 g of reactant) without solvent or in hydrocarbons in order to determine the isolated yields, and to characterize the products by ^1H and ^{13}C NMR spectroscopy as well as elemental analysis. The work up of the reaction turned out to be very simple: In the case of the solvent free reaction the product can usually be easily transferred by vacuum. In the case of the reaction with *o*-phthaladehyde the ester precipitates cleanly out of the solution. The extremely high TOFs for cyclohexanecarbaldehyde and 3-cyclohexanecarbaldehyde should be particularly noted. The reactions usually happen so quickly that only the product can be detected on NMR-scale reactions. The catalyst in the reaction solution is also still active after several days. Thus, a reaction that has subsided for some time can be restarted again by the addition of new reactant. Furthermore the suitability of **1a** for the dimerization of furfural should be emphasized, because up till now when this reaction is carried out with aluminum or tetracarbonylferrate catalysts either no or very low yields are observed. Although **1a** catalyzes the dimerization of aldehydes, with or without an α-H atom, quickly and in high yields, the reaction of butanal at 21 °C only higher coupling products are formed.[3b, 11] If one starts the reaction at – 78 °C then butyl butyrate and 2-ethyl-1,3-hexanediol monobutyrate as dimeric and trimeric products are yielded in almost the same ratio.[11a]

To present a provisional reaction mechanism, the dimerization of benzaldehyde was studied in more detail. ^1H NMR spectroscopy and GC/MS studies show that at the beginning of the reaction bis(trimethylsilyl)amine and benzylic acid bis(trimethylsilyl)amide are cleaved from **1** to give a lanthanide alkoxide **A** that is, most probably, the catalytically active species (Scheme 1). Investigations of the paramagnetic compound **1b** on catalytic and stoichiometric scales show that all three amide groups are cleaved without a significant induction time, and signals appear in the ^1H NMR spectra that may be attributed to $SmOCH_2$ groups. It can be assumed that the catalytically active species is either the same or very similar to the compound that is formed in the Tishchenko reaction with $[(C_5Me_5)_2LaCH(SiMe_3)_2]$.[5a] This hypothesis is supported by the following observations: 1) with **1a** similar yields are achieved as for $[(C_5Me_5)_2LaCH(SiMe_3)_2]$, which is, incidentally, significantly more difficult to prepare. 2) During the reaction both catalysts can completely interchange the whole of their original ligand shells. ^1H NMR spectroscopic investigations show, however, that from the reaction of **1b** with stoichiometric amounts of benzylalcohol or benzylaldehyde different compounds are formed. Kinetic investigations show

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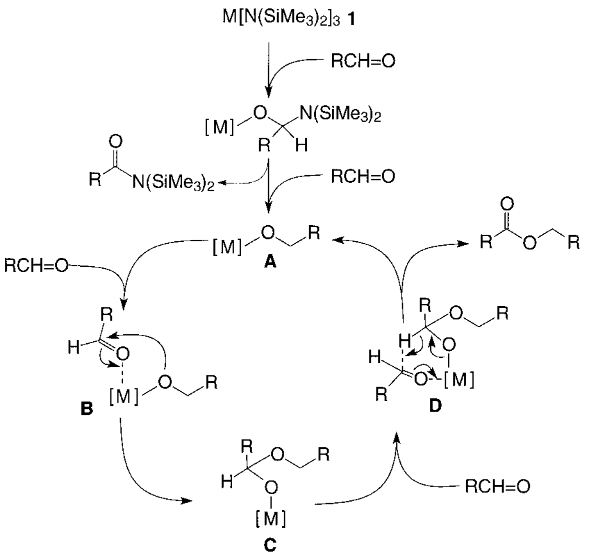

Scheme 1. Suggested mechanism for the $M[N(SiMe_3)_2]_3$-catalyzed Tishchenko reaction.

that 1/[reactant] is related linearly to the reaction time; that is, a second-order reaction with respect to the reactant occurs. Such reaction kinetics have already been established for the aluminum-catalyzed reaction for the dimerization of benzylaldehyde.[9] Presumably, a molecule of the reactant coordinates to **A** (→**B**), which in turn undergoes an alkoxide transfer (→**C**; Scheme 1). A second molecule of the reactant attaches itself to **C** followed by a hydride transfer that is probably the rate-determining step (→**D**).[9]

In summary it should be emphasized that the bis(trimethylsilyl)amide compounds of the lanthanides represent a new class of Tishchenko catalysts as a result of the high Lewis acidity and the easy interchangeability of the ligand sphere. These compounds are distinguished by a number of practical advantages such as the ease of accessibility (one compound can be bought), inexpensive metals, extremely high activities (to our knowledge there are no catalysts that are more active), and a high durability of the catalysts. These advantages lead us to hope that **1** , which is already today a standard reagent in organolanthanide chemistry, will find further application as a Tishchenko catalyst.

Experimental Section

NMR-scale reaction: Compound **1** (0.015 mmol) was weighed under protective gas into an NMR tube. C_6D_6 (≈0.7 mL) was condensed into the NMR tube, and the mixture was frozen at −196 °C. The reactant (1.5 mmol) was injected onto the solid mixture, and the whole sample was frozen at −196 °C. To determine the reaction kinetics the sample was melted and mixed just before the insertion into the core of the NMR machine (t_0). The ratio between the reactant (product) and the catalyst was exactly calculated by comparison of the integration of all C*H*O (C*H*$_2$O) signals with the N(Si*Me*$_3$)$_2$ signals. The latter were used as an internal standard for the kinetic measurements.

Preparative-scale reaction: a) without solvent: Under protective gas the catalyst (1 mol %) was stirred in a tempered reaction flask. The reactant (5 g) was added directly to the catalyst. Usually an exothermic reaction was observed. After one day the product was isolated by distillation. b) In solution: The catalyst (1 mol %) and the reactant (5 g) were each dissolved in pentane/hexane (1/1, 25 mL). The reactant solution was added together with the catalyst solution in a tempered flask. After one day the product was isolated by distillation.

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[10] As a catalyst for the dimerization of benzaldehyde, $Al(OCH_2Ph)_3$ is ten times faster than Al(O*i*Pr)$_3$, because here the metal has already exchanged all O*i*Pr for OCH_2Ph groups.[9] Although $Al(OCH_2Ph)_3$ is faster than Al(O*i*Pr)$_3$ for this reaction, one cannot assume that this is always the case. For our comparative studies we were not interested in a special reaction, but rather in a wider application. Thus the literature quoted is almost exclusively with Al(O*i*Pr)$_3$ as the catalyst.[3, 11a]

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$NaSn_5$: An Intermetallic Compound with Covalent *α*-Tin and Metallic *β*-Tin Structure Motifs

Thomas F. Fässler* and Christian Kronseder

Under standard conditions tin exists in the *β* modification, in which each tin atom is surrounded by six other Sn atoms in a distorted octahedral arrangement (Figure 1a, Scheme 1, Table 1). Below 13.2 °C transformation of *β*-tin into cubic *α*-tin (diamond structure), which is thermodynamically more stable by 2.09 kJ mol^{-1}, occurs.[1] In this modification, which has a lower density, all tin atoms are four-coordinate, and the structure can be described by invoking localized two-center, two-electron (2c–2e) bonds (Scheme 1). All structurally

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